Alternating Layers of Cationic and Anionic Supramolecular Polymers on Mica

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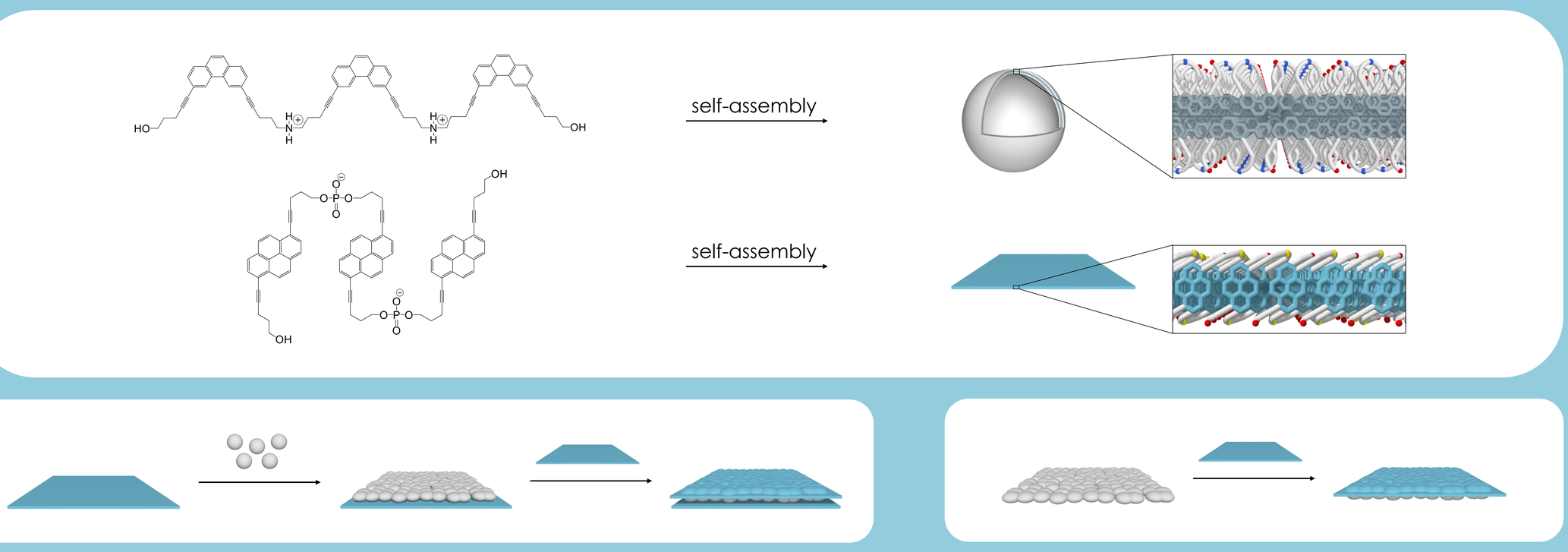
The self-assembly of 3,6-disubstituted amine-linked phenanthrene trimers with a positively charged backbone leads to the formation of vesicles in aqueous medium. In contrast, it was shown that 1,6-disubstituted phosphodiester-linked pyrene trimers, with a negatively charged backbone, self-assemble into sheets. The preformed cationic and anionic objects can be layered on top of each other. Sandwich-type structures of differently charged supramolecular assemblies were analyzed by atomic-force microscopy.

INTRODUCTION

Supramolecular layer-by-layer assembly is getting more and more interesting for the industry as it is a promising method for obtaining structured thin films on solid substrates. The well-controlled method enables to create electrostatically multilayered assemblies on a wide variety of substrates. In this work, mica was used as a solid substrate and the layers were analyzed by atomic-force-microscopy (AFM). The electrostatic interactions between the cationic and anionic molecules were utilized as a driving force for the self-assembly. By separately preforming the structures of the two molecules under optimized conditions, the assembly process was controllable and buffer independent.



MOLECULES

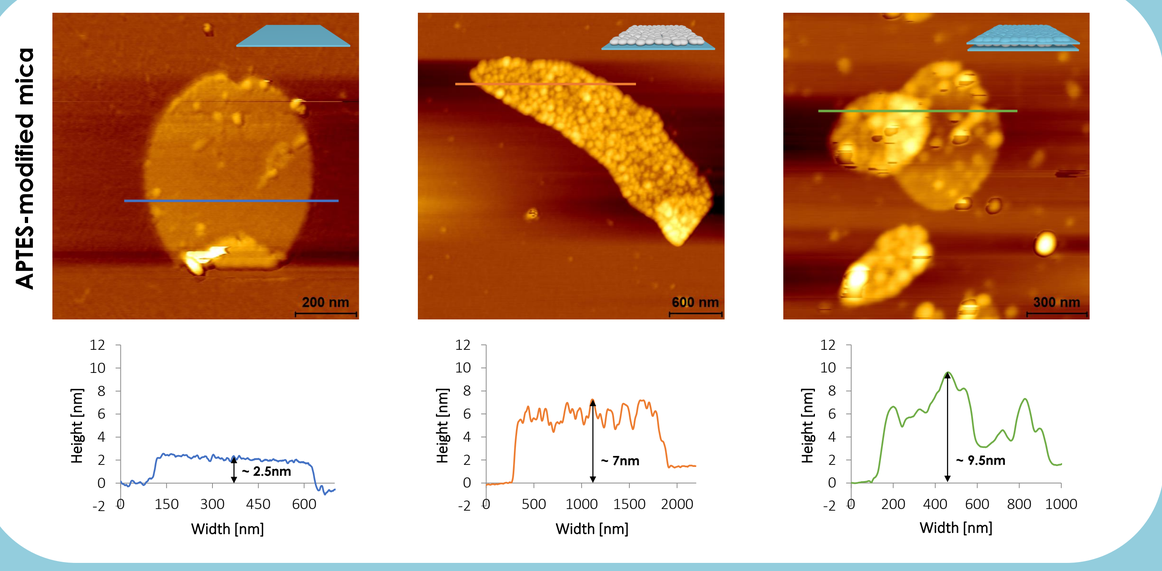
The 3,6-disubstituted amine-linked phenanthrene trimer (Phe_3) acts as a cation and the 1,6-disubstituted phosphodiester-linked pyrene trimer (Py_3) as an anion. The positive charge in the cation is induced in aqueous medium by the introduced amine in the linker, and the phosphodiester in the anion is responsible for the negative charge. Both molecules form different supramolecular polymers as shown in the upper figure. This simplifies the differentiation of the structures when measuring AFM.

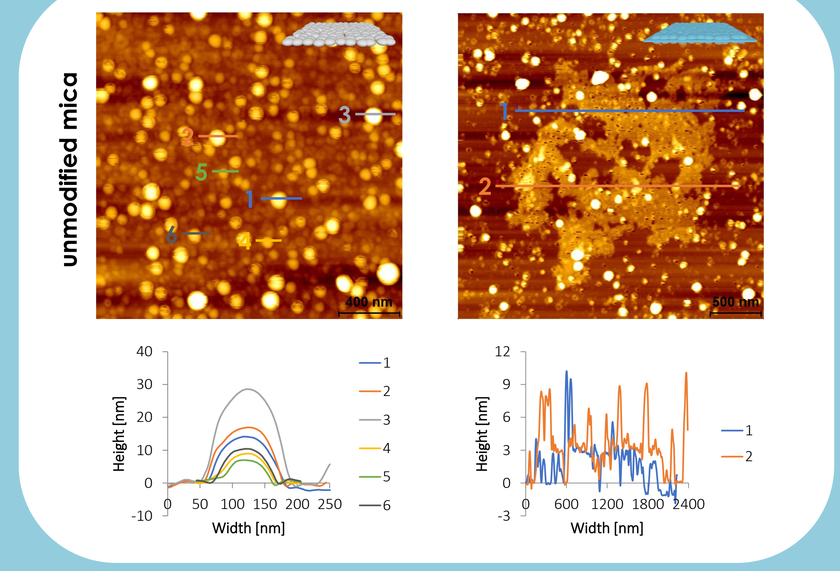
SUBSTRATE

Mica is used as a solid substrate. When the anionic supramolecular polymer is used as a first layer, the mica has to be modified so that it is positively charged. This is done by an APTES-modification of the mica-surface. On the other hand, if starting with the cationic species the mica can be used unmodified.

ATOMIC FORCE MICROSCOPY

The multilayered structures were analyzed by AFM. An advantage of their different self-assemblies was that they can be differentiated easily from each other. When starting with the Py_3-sheets it is possible to stack three layers on top of each other. The surface is afterwards too bumpy for a nice electrostatic attachment of another phenanthrene-vesicle layer. If starting with the Phe_3-vesicles so far only two layers are possible for the same reason as mentioned before. It seems like the vesicles are higher when adsorbing as the first layer on mica, than when being adsorbed on Py_3-sheets.





CONCLUSIONS

Two trimers, Phe_3 and Py_3, were successfully used for an alternating deposition of cationic and anionic supramolecular objects on mica. By self-assembly in an aqueous medium, two types of structures, vesicles and sheets, were preformed and further used for the assembly of layered structures. The driving force for the formation of these layers is their electrostatic interaction. AFM measurements, in particular the height profiles, nicely show the alternating layers. The vesicles appear smaller when adsorbed on the sheets than on pure mica. The challenge of both methods is the adsorption of vesicles on a bumpy surface. Further investigations are ongoing in changing the assembled structure of the cationic species.

References

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[2] M. Vybornyi, A. V. Rudnev, S. M. Langenegger, T. Wandlowski, G. Calzaferri, R. Häner, *Angew. Chem. Int. Ed.* **2013**, 52, 11488-11493.